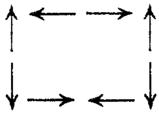
larity among the elements in the upper half is in the vertical direction, and in the lower half in the horizontal direction. This justifies the use of the expressions group-relation and period-relation. We may speak, therefore, of the *group-relation* of Cr, meaning its relationship to Mo and W, and to a less degree to S; and of the *period-relation* of Cr, indicating its connection to Mn, Fe, etc. From the fact that the elements of the subperiods III′, IV′ and V′ have many polar numbers in common, *e. g.*, 2 and 3 in III′, 2 and 4 in IV′, etc., we may deduce an explanation for their similarity.

Another advantage of the table is that the numerical values expressing certain properties (melting point, atomic volume, etc.) are easily inserted and that the relationship between these factors is much better shown, for the elements are better separated (Mn, for example, does not come between Cl and Br as in the old table) and the direction of the increase or decrease of the values can be expressed by arrows placed on the border of the table. I have prepared such tables for a very large number of different properties, and find that the arrows indicate in a very clear way the general trend. Thus the scheme for the specific gravity would show the following arrows on the border of the table:



indicating clearly that the alkali metals are the lightest, and the platinum metals the heaviest.

In order to place the isotopes of the radioactive elements it will be necessary to place the top row from lead to thorium at the bottom of the table, extending the row on both sides, so as to include the elements with atomic numbers 81 to 92. Under this line the system of the radioactive elements can be placed, which then will form a kind of appendix to the main table.

Berkeley, Cal.

THE COLLOIDAL PRODUCTS OF THE REACTIONS BETWEEN POTASSIUM DICHROMATE AND STANNOUS SALTS.

By J. C. Witt.

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When normal potassium dichromate solution is added to normal stannous chloride solution in equivalent proportions, brownish and greenish blue gelatinous masses are formed. At one point during the addition the entire mixture becomes a gel and a considerable rise in temperature is noted. When all the dichromate has been added, the brownish tinge gradually disappears, and in time the whole reaction mixture becomes a clear, deep olive-green, which in sufficient depth appears red by transmitted light, either natural or artificial.

This peculiar behavior has been described in a previous paper[1] and seemed to merit further investigation. It was desired to learn the composition of the brown intermediate substance and the cause of the appearance and disappearance of the various colored gels. At first it seemed apparent that the brown substance was in some way formed by a reaction between stannous chloride and potassium dichromate, in which the former was in excess, because it always appeared before an equivalent amount of the latter had been added, and gradually disappeared after the 2 substances were present in equivalent proportions. On this basis, however, no explanation was apparent why it was never possible to obtain the brown substance by treating stannous chloride with the equivalent amount of dichromate in the absence of acid. This experiment was repeated several times with negative results, but on adding an excess of dichromate, a brown precipitate at once appeared. A number of titrations were then made in which various quantities of excess of dichromate were added. In each case the precipitate was collected and dissolved in hydrochloric acid and the dichromate it contained was determined. The unreduced dichromate in the filtrate was also determined after addition of hydrochloric acid. The results are shown in Table I.

TABLE I.—EFFECT OF ADDING EXCESS POTASSIUM DICHROMATE TO STANNOUS CHLORIDE IN ABSENCE OF ACID.

10 cc. of Stannous Chloride taken: 9.60 cc. of *N* Dichromate Solution Required for End-point.

Excess dichromate added. Cc.	Dichromate found.			Appearance of filtrate.	Amount of precipitate.
	Fltrate. Cc.	Precipitate. Cc.	Total. Cc.		
4	4.25	0.09	4.34	Very dark	Trace
5	3.12	2.03	5.15	Dark	Small
6	4.48	1.54	6.02	Turbid	Small
7	3.56	3.38	6.94	Yellow and clear	Heavy
8	3.97	3.93	7.90	Yellow and clear	Heavy

A study of this table reveals a number of interesting points. On comparison of Cols. 1 and 6, it appears that, if excess of dichromate up to 6 cc. is added, only slight precipitation occurs, whereas 7 cc. or over suffice to produce heavy precipitation. Comparison of Cols. 1 and 4 shows that the excess of dichromate distributed between precipitate and filtrate has suffered no change in its oxidizing power—a result indeed that one might have expected, since no reducing agent was present. It is improbable that the presence of dichromate in the precipitate is due to formation of any insoluble dichromate by metathesis; hence, the more probable

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[1] For previous work with this class of reactions, see M. Neidle and J. C. Witt, THIS JOURNAL, **37,** 2360 (1915); **38,** 47 (1916); M. Neidle and J. N. Crombie, *Ibid.*, **38,** 2607 (1916).

explanation of the formation of the precipitate and the presence of dichromate in it is that the colloidal hydrous oxides of chromium and tin have been precipitated by the electrolyte, potassium dichromate, and that considerable of the latter has been adsorbed. The second and third numbers of Col. 3 show a discrepancy in increase of dichromate content of the precipitate, and this may be due in some manner to incipient precipitation of the gel.

On this basis, the explanation of the appearance and disappearance of the gel during the mixing of the 2 solutions is simple. The solutions were brought together in a flask and no special care was taken to mix the contents thoroughly. Thus the dichromate was present in excess at some points even before the total amount added was sufficient for complete oxidation of the stannous salt. This excess of dichromate precipitated the colloids at various points in the solution, and produced the peculiar mottled appearance which has been described. If, after addition of the equivalent of dichromate, the mixture was allowed to stand, the remainder of the stannous chloride present gradually removed the dichromate from the precipitate and the colloid was regenerated, producing a homogeneous green liquid.

The precipitation of the colloids from the reaction mixture by potassium dichromate suggested that a like precipitation might be produced by other electrolytes. The mixture was therefore tested with a number of them, care being taken to choose only those which would not produce insoluble compounds with any of the ions present in the solution. It was found that the precipitating power of all the electrolytes tried depended on the valence of the anion but was independent of the valence of the cation. The colloids were precipitated whenever an added electrolyte contained an anion with a valence greater than one. The sol obtained by dialyzing the reaction mixture showed the same characteristics, except that in every case a smaller amount of the electrolyte was necessary to produce precipitation.

Reaction between Potassium Dichromate and Stannous Sulfate.—The fact that the colloids were precipitated by anions having a valence greater than one, and the difference between the behavior of ferrous chloride and that of ferrous sulfate when oxidized with potassium dichromate[1] suggested that if a stannous salt having a bivalent anion were used in place of stannous chloride, the colloids produced would not form a sol but would be precipitated immediately.

Stannous sulfate was prepared by dissolving metallic tin in conc. sulfuric acid and purifying the salt by crystallization. When normal potassium dichromate was added to an approximately normal solution of the stannous sulfate, a green precipitate at once appeared and increased in

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[1] THIS JOURNAL, 37, 2360 (1915).

volume until the end-point was reached. Further addition of dichromate did not yield a brown precipitate as was the case with stannous chloride. In further investigation of the reaction, 25 cc. of the stannous sulfate solution was treated with an equivalent amount (24.86 cc.) of normal dichromate solution. The precipitate formed was collected and washed several times. The filtrate was analyzed for chromium, potassium, and sulfate—it contained no tin. The stannous sulfate solution had been previously analyzed and the concentration of the dichromate solution was known. From these data, the composition of the precipitate was calculated. These values are shown in Table II.

TABLE II.—SHOWING TOTAL AMOUNT OF EACH CONSTITUENT IN 25 CC. STANNOUS SULFATE, IN THE EQUIVALENT AMOUNT OF POTASSIUM DICHROMATE, AND IN THE FILTRATE AND PRECIPITATE RESULTING FROM MIXING THE TWO.

Constituent.	Potassium dichromate (calc.).	Stannous sulfate (by analysis).	Filtrate (by analysis).	Precipitate (by difference).
Cr	0.4310	..	0.1242	0.3068
K	0.3241	..	0.3218	0.0023
Sn	..	1.4880	0.0000	1.4880
SO_4	..	1.3020	0.7979	0.5041

A study of this table reveals that the reaction with stannous sulfate is essentially similar to that with the chloride. All the tin remains in the precipitate and practically all the potassium is found in the filtrate, whereas the chromium and sulfate are distributed between precipitate and filtrate. The amount of chromium in the precipitate is greatly influenced by the dilution of the 2 solutions at the time of mixing. Normal dichromate and normal stannous sulfate solutions, run simultaneously into a relatively large volume of water, yield a filtrate containing much less chromium.

Titrations of the stannous sulfate with potassium dichromate were made with and without an excess of sulfuric acid, to determine if there was any difference in the results, as was the case with ferrous sulfate and potassium dichromate.[1] Each of four 10 cc. portions of stannous sulfate solution was diluted with 100 cc. of water. To each of 2 of them was added 5 cc. of conc. sulfuric acid. All 4 were titrated with potassium dichromate, a mixture of potassium thiocyanate and ferrous sulfate being used as an outside indicator, with the following results: in presence of acid 10.35 and 10.42 cc., and in absence of acid 9.94 and 9.95 cc. were required.

At first it seems that the discrepancy in the titrations in absence of acid is the reverse of that found with ferrous sulfate, since in the latter case the titrations without acid were higher than those with acid. However, this difference can be easily explained by considering the indicators used in

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[1] *Loc. cit.*

each case. With the ferrous sulfate titrations, the end-point is reached when the ferrous ion is no longer present in sufficient concentration to affect the potassium ferricyanide indicator; whereas, with the stannous sulfate the end-point is reached only when there is sufficient concentration of dichromate ions present to oxidize the ferrous sulfate in the indicator, whereby a red coloration with the potassium thiocyanate is produced. This means that for some reason not all of the stannous ions present are active in reducing the dichromate, since, otherwise, no end-point could be obtained until the theoretical amount of dichromate solution had been added.

A series of titrations was made to determine whether or not the end-point is influenced by the concentration of the stannous sulfate solution. Five cc. portions of the stannous sulfate solution, diluted with varying quantities of water, were titrated with 0.2 *N* dichromate, in the absence of acid. Five cc. of the stannous solution containing excess acid required 25.35 cc. of dichromate solution. Without acid, and with the addition of 0, 10, 20, 50, 100, 500 cc. of water, the titrations were 24.19, 24.37, 24.57, 24.56, 24.29, 22.21 cc., respectively. If these results were in conformity with the results obtained with ferrous sulfate under similar conditions, allowing for the difference in producing the end-point, the titrations should show constantly decreasing values with increase in dilution of the stannous sulfate solution. It can be seen that this is not true. In several cases after the titration had been completed the precipitate was collected and dissolved in sulfuric acid and the solution diluted to 100 cc. The filtrate was acidified with sulfuric acid and both solutions were then titrated with dichromate.[1] In every case, the filtrate was capable of affecting the indicator without further addition of dichromate. The titration of the dissolved precipitate was practically the same as the difference between the original acid and non-acid titrations.

The interpretation of these results is that in the case of stannous sulfate the discrepancy between the acid and non-acid titration is brought about principally by the adsorption of the stannous ion by the precipitated colloids and not to any great extent by the difference in speed of the reaction, as was found to be the case with ferrous sulfate.

MANILA, PHILIPPINE ISLANDS.

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[1] It was found that the sulfuric acid alone produced a slight red coloration with the indicator. This was prevented by adding a few pieces of metallic zinc to the acid shortly before using it.